

Probing ultrafast symmetry breaking in photo-stimulated matter

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Picosecond Raman scattering is used to study the photo-induced ultrafast dynamics in Peierls distorted Antimony. We find evidence for an ultrafast non-thermal reversible structural phase transition. Most surprisingly, we find evidence that this transition evolves toward a lower symmetry, in contrast to the commonly accepted rhombohedral-to-simple cubic transition path. Our study demonstrates the feasibility of ultrafast Raman scattering symmetry analysis of photo-induced non-thermal transient phases.

Controlling the state of a material through light irradiation and thereby obtaining transient highly-off-equilibrium phases, is one of the intriguing achievements in condensed matter science of the last decade.[1, 2, 3] Progress in this field has been boosted by the easy availability of extremely short light pulses (10^{-14} s), kindling the hope of controlling matter on ultrafast time-scales, *i.e.* on timescales faster than the characteristic thermodynamical timescale which limit the speed of current phase change media based devices. The main emerging limitation in bidirectional ultrafast optical switching is that by and large the photo-induced phase transitions reported to date are low to high symmetry transitions. Rare are the examples of photo-induced high to low symmetry transitions necessary to complete the ultrafast bidirectional switching cycle and controversial the possibility of photo-inducing a high to low symmetry phase transition on ultrafast timescales[4, 5], while the low-to-high symmetry phase transition can occur through direct coupling of the the light field (carrying little momentum) to crystal excitations, the reduction of the symmetry can only arise due to a cooperative effect leading to self-organized long-range order which is usually limited to occur on 'thermodynamic' timescales. In contrast to this, our findings from ultrafast experiments on the A7 metals demonstrate the possibility of inducing a reversible photo-induced symmetry lowering on timescales surpassing the time needed to reach thermodynamical equilibrium.

The group V semi-metals like Bismuth and Antimony have served as a playground for studying interactions between ultrafast light pulses and absorbing matter.[6, 7, 8, 9] The strong coupling between the structural and electronic degrees of freedom in these materials allowed for the first pioneering studies in the late-eighties, early-nineties on "coherent phonon" generation in absorbing materials, visualizing the real time behavior

of optical phonons.[10, 11, 12] More recently the structural and electronic dynamics following laser irradiation in Bi and Sb single crystals have been studied in great detail, and the possibility of inducing a "non-thermal" phase transition to a simple cubic phase has been discussed on the base of ab-initio calculations.[13, 14, 15, 16] The structure of the A7 compounds (sketched in Fig.1a) may be described as a distorted simple cubic structure, where the (111) planes of atoms have an alternating displacement along the [111] direction. This structural peculiarity of the semi metals Bi, Sb, and As has been widely discussed in the past[17, 18, 19], and originates from a strong electron phonon coupling. In one dimension, this type of distortion is the well known Peierls distortion.[20, 21]

The physics behind the expected photo-induced effects in A7 metals can be sketched in a simple way. The photo-excitation of valence band electrons increases the electron density in the conduction band and, as a consequence, it reduces the energy gain of the Peierls distortion. Eventually this renders the Peierls distortion unstable, and a phase transition should occur to the undistorted phase on a time-scale faster than the time required for electron-phonon thermalization. The ab-initio calculations mentioned earlier indicated that the cubic phase should be reached for a critical excitation density of 2.7 electrons per hundred ions.[13, 16] Various experimental studies have tried to reach this excitation limit and to detect an optically induced phase transition in Bismuth and Antimony single crystals making use of a variety of techniques, including time-resolved reflectivity,[22] x-ray diffraction,[15, 23] and UV absorption experiments.[24] In spite of the experimental efforts devoted, no evidence of an optically induced reversible phase transition in the A7 semimetals has been reported so far under any of the explored excitation conditions.

The current work presents results of an ultrafast time resolved Raman spectroscopy study of Antimony single crystals [28]. This technique is sensitive to transient changes in the crystal structure through transient changes in the spontaneous vibrational Raman response. In addition to this, a comparison between the Stokes and anti-Stokes scattering intensity allows to distinguish the

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dynamics induced by lattice heating effects from the non-thermal ones arising from the electronic screening of the crystal potential. The experiments reveal two distinct dynamics: A fast non-thermal response occurring in the first few picoseconds after irradiation, and a slower thermal one which lasts for more than 100ps. The short time response evidences the existence of an induced transient state, even though the nature of this state deviates from the expected simple cubic phase.

The experiments were performed using a 80 MHz picosecond Ti:Sapphire laser (MIRA 900, wavelength 800 nm, pulse duration 1.7 ps) as excitation laser, which was coupled using a custom designed pump-probe scheme, to the microscope of a standard charge coupled device equipped Raman spectrometer (T64000, Jobin Yvon). All experiments have been performed at ambient conditions in a controlled Argon environment.

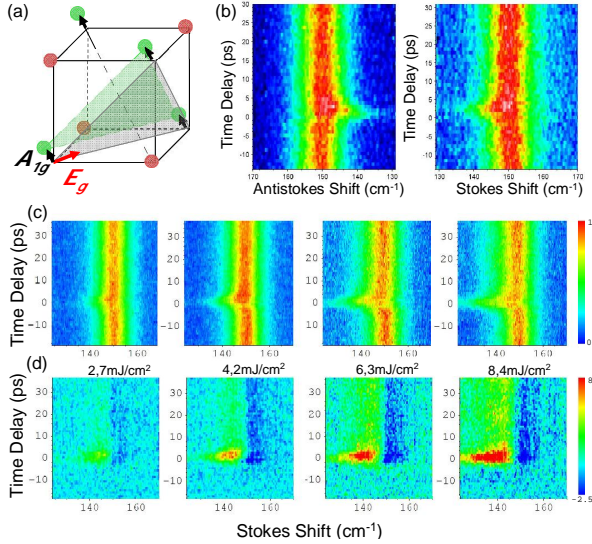


FIG. 1: (a) Equilibrium structure of the A7 semimetals (space group $R\bar{3}m$). The A_{1g} vibrational mode corresponds to a modulation of the distance between the (111) planes, while the E_g mode corresponds to a sliding of adjacent (111) planes. (b) False color plot of the time resolved Stokes (left) and anti-Stokes (right) Raman data for excitation density of 4.6 mJ/cm^2 . (c) False color plot of the pump-probe Raman data for various pump intensities. (d) Optically induced changes in the Raman spectra obtained by the subtraction of the negative time response from the data in (c).

Fig.1(b) shows the time evolution of the A_{1g} mode in Antimony after excitation with a moderately low pump power density (4.6 mJ/cm^2). The right and left panels display a false color plot of the Stokes and anti-Stokes response, respectively. In the first few picoseconds after excitation, the A_{1g} mode shows a rapid and appreciable softening toward the low energy side, with a subsequent relaxation, in roughly 10 ps, to a transient spectrum which is close to the equilibrium one. This transient state slowly relaxes to the equilibrium situation, with a

decay time exceeding 100 ps. The dynamical response is demonstrated more clearly in Fig. 1(c) and (d), which display in a false color plot the direct (b) and differential (c) transient Stokes response for four different excitation densities.

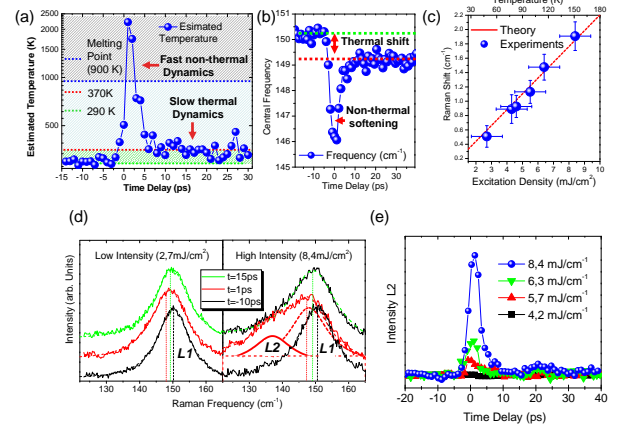


FIG. 2: (a) Time evolution of the A_{1g} phonon temperature after excitation with 4.6 mJ/cm^2 . The blue dashed line indicates the thermodynamical melting temperature. The average long time laser induced heating is indicated by the red dashed line. (b) Time evolution of the central frequency of the Stokes line for a pump excitation of 4.6 mJ/cm^2 . (c) Thermal frequency shift of the A_{1g} phonon at 20 picoseconds after pump excitation versus the pump excitation density and the expected temperature variation. The dashed red line shows the temperature dependence of the frequency shift obtained from continuous wave experiments. (d) Raman response for the unperturbed system ($t=-10$ ps, black curve), for the ultrafast non-thermal response ($t=1$ ps, red curve) and for the thermal response ($t=20$ ps, green curve). The left and right panels depicts Raman spectra in the low and high excitation density limit, respectively. (e) Time traces of the intensity of the new phonon line for various excitation densities.

The ratio of the intensity of the Stokes and anti-Stokes spectra allow extraction of the non-equilibrium phonon temperature as a function of time. The evolution of the phonon temperature after the pump excitation with a density of 4.6 mJ/cm^2 is depicted in Fig.2(a). In the first 3 ps the phonon temperature raises to more than 2000 K. Clearly this does not correspond to a thermodynamic temperature raise, but merely reflects the non-equilibrium phonon occupation which is boosting the anti-Stokes response. On the same timescale, however, also the frequency of the A_{1g} mode softens considerably (see Fig.2(b)) to values which are not achievable under equilibrium conditions (at atmospheric pressure[25]). This indicates that not only population effects, but also electronic screening occurs on this timescale. We will return to discuss the fast response later on after having discussed the nature of the spectral changes at large positive times ($t > 10$ ps).

Equilibrium between the electronic and the lattice tem-

perature is reached in about 10 picoseconds after pump irradiation. Based on the equilibrium thermodynamical and optical properties of Antimony, one can estimate the expected temperature raise resulting from the photo excitation. As an example, based on the reflectivity, optical penetration depth, and heat capacity of Antimony, one expects that excitation with a power density of 4.6 mJ/cm^2 results in a temperature raise of approximately 80K. This is indeed what is observed experimentally, as is indicated by the red dashed line in Fig.2(a). The temperature raise estimated from the intensity of the anti-Stokes signals is confirmed by the frequency shift of the A_{1g} phonon, as is indicated by the red dashed line in Fig.2(b) which indicates the expected frequency for Sb at $T = 370 \text{ K}$ [26]. The residual frequency shift observed at times larger than 10 ps confirms the completed thermalization between the electronic and lattice subsystems. This is further illustrated in Fig.2(c), which compares frequency of the A_{1g} mode as a function of the measured phonon temperature at 20 ps after excitation (symbols) with the result of continuous wave Raman measurements as a function of the thermodynamic temperature[26] (red line). The good agreement of the experimental and estimated temperature (at long times $>10 \text{ ps}$) indicates that diffusive heat transport by photo-excited electrons is less efficient than energy relaxation to the lattice. Nearly all the energy dumped by the optical pulse and adsorbed by the electronic subsystem results in local lattice heating within 10 ps. Vibrational and electronic heat diffusion only play a significant role at later times when the system slowly relaxes back to the initial state ($t > 100 \text{ ps}$).

Now we turn to back to the ultrafast response. Two features clearly evidence the non-thermal nature of the processes occurring at early times following laser irradiation. Firstly the calculated phonon temperature in the first 10 picoseconds reaches values up to 2200 K, well above the equilibrium melting temperature of Antimony (indicated by the blue dashed line in Fig.2(a)). Secondly, the frequency of the A_{1g} mode in the first 10 picoseconds reaches values lower than those measured under equilibrium conditions at any temperature up to the melting point. The observed non-thermal phonon softening is comparable to the one measured in the time-domain with similar electronic excitation densities, clearly demonstrating that the electronic screening of the crystal potential induces a large phonon softening and that anharmonicity only plays a minor role, if any.

One of the most striking observations is that the line shape for the first few picoseconds after excitation is substantially different for low and high excitation densities. This is illustrated in Fig.2(d), where the upper and lower panels show the Raman response in the region of the A_{1g} mode at different times for low (2.7 mJ/cm^2) and high (8.4 mJ/cm^2) excitation density, respectively. Both before arrival of the pump pulse (black traces) as well as at late times (green traces) the phonon response shows

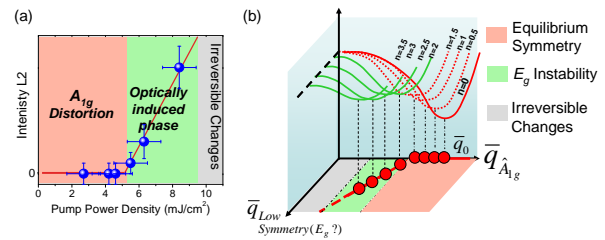


FIG. 3: (a) Maximum intensity of the new vibrational mode (L2) of the induced phase as a function of pump power density. (b) Sketch of the induced non-linear dynamics in the A7 metals. The curves represent cuts of the free energy for a distortion along the A_{1g} direction. For low density electronic excitation the minimum of the free energy stays on the fully symmetric (A_{1g}) direction thereby preserving the A7 symmetry. Excitation densities exceeding 2 electron per 100 atoms (5 mJ/cm^2) lead to a symmetry breaking due to displacement along a low symmetry direction (possibly E_g).

the standard Lorentian distribution (L1) for both excitation densities. In contrast, the early time responses (red traces) differ drastically. For moderately low power density ($<5 \text{ mJ/cm}^2$) the A_{1g} phonon shifts to lower frequency, keeping a Lorentian shape response with approximately the same linewidth as measured before pumping, indicating that the A7 structure is retained. This is no longer true for power densities exceeding 5 mJ/cm^2 . In this case the early time Raman spectrum shows, apart from the normal response (L1) the appearance of a new shoulder (L2) at the low energy side. This strongly suggests that at high excitations density the symmetry of antimony has changed substantially in the first few picoseconds, *i.e.* that an optical phase transition has occurred. Further strong evidence for this comes from the threshold behavior observed in the activation of the L2 mode as demonstrated in Fig. 3(a). The mode is only observed for excitation densities exceeding 5 mJ/cm^2 , and shows a linear increase of intensity upon further increasing the excitation density.

A two component fit of the high excitation density Raman spectra at different delay times reveals that the additional phonon mode, unlike the L1 mode, has a time independent frequency. Moreover, the frequency of the new mode is $\simeq 10\%$ lower than the frequency of the equilibrium A_{1g} mode, and $\simeq 20\%$ higher than the E_g mode. This latter mode, which is active in a different scattering geometry, could be activated by optically induced disorder. These observations demonstrate that this new mode is indeed not originating from the A7 structure. Finally we note that the optically induced phase has a relatively short lifetime ($\sim 5 \text{ ps}$) as shown by the time dependence of the intensity plotted in Fig.2(e).

The question now arises what the symmetry of the new optically induced phase is. It is clear that the long expected phase transition to the high symmetry cubic

phase can be excluded. For the simple cubic symmetry one expects no optical phonon mode at all, in striking contrast with the presence of the observed additional mode. Moreover, one would expect a complete softening of the A_{1g} mode which is clearly not observed. No anti-correlation between the intensities of the L1 and L2 modes has been observed. This makes it unlikely that the observed new mode is due to a new phase which coexists with the A7 structure. We therefore conclude that both observed modes originate from the optically induced phase, and that this phase has a lower symmetry than the A7 structure. One intriguing possibility is that the structural change is not due to a softening of the A_{1g} mode, but rather due to a E_g distortion, *i.e.* due to an alternating displacement of the (111) planes along a direction perpendicular to the [111] direction (indicated in Fig.1a). Such a distortion would most likely lead to a monoclinic $C2/m$ structure, with indeed an activation of additional modes in the Raman spectrum.[29]

Fig.3 (b) summarizes the mechanism suggested for the optically-induced phase transition in the A7 metals. The excitation of electrons into the conduction bands reduces the energy gain of the Peierls distortion forcing the ions to move towards the cubic undistorted symmetry (red area in Fig.3 (a) and (b)). As the excitation density is increased the alternating distortion of the (111) planes along the A_{1g} direction reduces while retaining the overall rhombohedral symmetry. For excitation densities exceeding $\sim 5\text{mJ}/\text{cm}^2$ an instability (possibly of E_g nature) sets in (green dashed area in Fig.3 (a) and (b)) which reduces the A7 symmetry without ever reaching the high symmetry cubic phase. We believe that in our configuration we can explore this region of the phase diagram thanks to the fact that our measurements do not require the non-adiabatic coherent excitation of the fully symmetric A_{1g} mode for detection. The collectiveness of the coherent excitation of a fully symmetric mode could increase the energy cost of displacing the ions towards a lower symmetry location and would indicate why such a transient response has never been observed with different techniques.

In conclusion we demonstrated the feasibility of time resolved Raman studies to unravel the interplay between electronic and structural degrees of freedom. Insight into the thermalization processes between electrons and ions have been obtained from the measured transient Raman spectra, showing the thermal nature of the crystal response for times larger than 10 picoseconds after the pump excitation, and demonstrating that electronic energy diffusion plays a minor role in the transient dynamics for the A7 metals. In the non-thermal region ($t < 10$ picoseconds) we demonstrate that the electronic screening of the crystal potential can induce a large phonon softening ruling out that anharmonicity plays an important role. Maybe the most important result of the present work is the observation of an ultrafast optically

induced phase transition toward a non-thermal low symmetry phase for excitations exceeding 2 electron per 100 ions. Ultrafast symmetry lowering transitions are important for ultrafast bidirectional switching and contrasts most of the observed ultrafast phase transitions to date.

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 - [29] The dispersion relations of the E_g modes in Antimony single crystal[27] show that a doubling of the unit cell would give an additional zone center mode at a frequency close to the observed one.